

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
17 October 2002 (17.10.2002)

PCT

(10) International Publication Number  
WO 02/081379 A1

(51) International Patent Classification<sup>7</sup>: C02F 1/02

(21) International Application Number: PCT/KR02/00592

(22) International Filing Date: 3 April 2002 (03.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2001/18038 4 April 2001 (04.04.2001) KR

(71) Applicant (for all designated States except US): HAN-WHA CHEMICAL CORPORATION [KR/KR]; 1, Janggyo-Dong, Jung-Gu, 100-797 Seoul (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HAN, Joo-Hee [KR/KR]; 209-1703, Expo Apt., Jeonmin-Dong, Yusung-Gu, 305-761 Taejon (KR). NOH, Min-Jeong [KR/KR]; 107-1303, Expo Apt., Jeonmin-dong, Yusung-ku, 305-761 Taejon (KR). CHOI, Young-Jae [KR/KR]; 107-901, Dure Apt., Sinsung-Dong, Yusung-Gu, 305-720 Taejon (KR). SHIN, Young-Ho [KR/KR];

110-107, Dure Apt., Sinsung-Dong, Yusung-Gu, 305-720 Taejon (KR). CHUNG, Chang-Mo [KR/KR]; 106-1003, Luckyhana Apt., Sinsung-Dong, Yusung-Gu, 305-721 Taejon (KR). HAN, Gi-Woo [KR/KR]; 210-89, Sinsung-Dong, Yusung-Gu, 305-345 Taejon (KR).

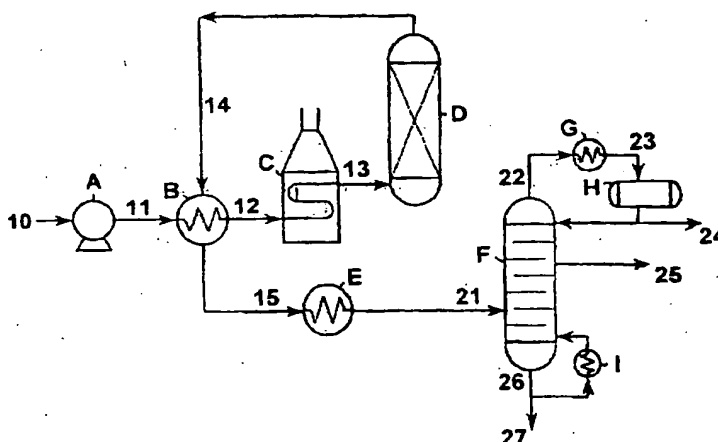
(74) Agents: LEE, Chul et al.; 2F, Changsang Building, 1543-12, Seocho-3dong, Seocho-ku, 137-872 Seoul (KR).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PROCESS FOR TREATING WASTE WATER CONTAINING A NITROUS ORGANIC COMPONENTS



(57) Abstract: Disclosed is a process for treating waste water containing nitrous organic components, comprising the steps of : feeding pressurized waste water stream of 130-250 atm to a hydrolysis reactor, in which the pressurized waste water stream is heated during feeding to the reactor by heat exchange with the hydrolyzed stream; hydrolyzing the nitrous components in the waste water stream by heating it to the liquid phase temp. range of 200-370°, which is below a critical point of water; transporting the hydrolyzed stream to a distillation column, in which the hydrolyzed stream is cooled during the transportation to the distillation column by heat exchange with the pressurized waste water stream to be fed into the hydrolysis reactor; and recovering ammonia as an overhead fraction, aqueous solution containing ammonia and carbon dioxide as a side fraction, and the remainder removed of ammonia and carbon dioxide as a bottom fraction, respectively, from the distillation column.

BEST AVAILABLE COPY

WO 02/081379 A1



**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## PROCESS FOR TREATING WASTE WATER CONTAINING A NITROUS ORGANIC COMPONENTS

### TECHNICAL FIELD

The present invention relates to a process for treating waste water containing  
5 nitrous organic components. More specifically, this invention pertains to a process  
for treating waste water containing nitrous organic components, in which the waste  
water containing the nitrous organic components is hydrolyzed under conditions of  
temperature and pressure close to a critical point of water so that the nitrous organic  
components in the waste water are decomposed to ammonia and carbon dioxide, and  
10 then ammonia and carbon dioxide are recovered for using as raw materials.

Particularly, the present invention is a technology useful to treat a high  
concentration waste water containing refractory nitrous organic components, which is  
difficult to biologically treat, and which can be usefully applied to a near-critical water  
hydrolysis and ammonia recovery process, in which the organic components are  
15 hydrolyzed under conditions of temperature and pressure close to a critical point of  
water to ammonia and carbon dioxide, and then ammonia and carbon dioxide are  
recovered for using as raw materials. In addition, the process for treating waste water  
containing nitrous organic components according to the present invention enables  
ammonia and carbon dioxide to be used as raw materials in a process for synthesizing  
20 urea by recovering ammonia and carbon dioxide after the nitrous organic components  
are decomposed, and the treated water to be used as process water, thereby occurring  
of the waste water may be originally prevented.

### PRIOR ART

Industrial waste water is a representative example of side products occurring  
25 with the advance of an industry. Recently, a biological treatment for treating  
industrial waste water has been widely used, but it cannot be usefully applied to treat  
the waste water or liquid containing high concentration, refractory, or toxic organic

components. In particular, most of nitrous organic components are refractory. Even though being decomposed, they are easily reduced to ammonia or oxidized to nitric acid, which causes additional problems in the ecosystem. The nitrous organic components dissolved in water may serve as a nutrient for microbes at a low concentration. On the other hand, when the concentration is high, aquatic life's existence is threatened because oxygen in water is exhausted owing to drastic increase of phytoplankton. In addition, the nutrient excessively contained in water causes secondary pollution such as green tide and red tide. Furthermore, ammonia or nitric ions dissolved in water have undesirable effects on the ecosystem due to toxicity thereof.

Nitrogen contained in waste water is classified into nitrate nitrogen, ammoniacal nitrogen, and organic nitrogen. Total content of these three kinds of nitrogen is called total nitrogen content, and the total nitrogen content of treated water to be discharged is restricted by laws.

Conventionally, there are physical and chemical treatments for removing nitrogen. The physical treatments are exemplified by ion exchange and ammonia stripping methods. As for chemical treatments, a treatment for removing ammonia using a chlorination reaction, a biological treatment, and an incineration treatment have been known in the art.

According to the ion exchange treatment, a selective ion exchange treatment is suggested, in which ammonia ions are removed by use of cation exchange resin, or nitric ions are removed by use of anion exchange resin. However, it is difficult to treat concentrated waste water which is produced during the regeneration of the ion exchange resin. Further, when organic components are contained in water at high concentrations, the removal of nitrogen and organic components is very difficult. Therefore, it is not preferable for this treatment to be solely applied to waste water containing a large amount of organic nitrogen.

The ammonia stripping treatment removes gaseous ammonia by contacting the waste water with air while the waste water maintains pH of 10.5 to 11.5. However, this method is disadvantageous in that time for removing ammonia is too long, and the treatment cost is relatively high because ammonia is re-separated from moisture in gas

phase. Furthermore, nitrous components other than ammonia and organics in waste water cannot be removed.

5 In the case of the treatment for removing ammonia by use of a chlorination reaction, waste water containing ammonium ions is added with chlorine to produce nitrogen gas and hydrochloric acid, thereby ammonia can be removed. However, this treatment is disadvantageous in that safety in work operations is threatened because excessive chlorine is used for removing ammonia, remaining chlorine in water should be again removed, and organic nitrogen is hard to remove.

10 The treatment for biologically removing organic components and nitrogen by use of nitrifying organisms and denitrifying organisms is useful to treat large quantities of sewage because of low operation costs. But, such treatment cannot be suitably applied to industrial waste water containing high concentrations of chemicals toxic to a microorganism, which requires a long treatment time, even though the treatment can be effectively applied to a domestic sewage in which toxic nitrous organic component  
15 is contained in small amounts. In other words, the treatment requires a long time because decomposition rate of pollutants by the microorganism is slow, and cannot be suitably applied to the industrial waste water, which is suddenly changed in organic components concentration according to chemical process conditions, because the microorganism does not sufficiently cope with sudden changes of the organic  
20 components concentration.

Most widely used to treat wastes containing high concentrations of nitrous organic components is the incineration treatment. But, this treatment has disadvantages in that nitrogen oxide ( $\text{NO}_x$ ) is discharged during the incineration of wastes, and a lot of energy is consumed. Accordingly, an additional catalytic reactor  
25 should be equipped for removing  $\text{NO}_x$ , which incurs high treatment cost and makes the operation too complex. In addition, the incineration treatment causes secondary pollution and high energy consumption, and thus is being gradually substituted with a novel treatment in advanced countries.

Much effort has been made to avoid the above problems. For example,  
30 reference may be made to U.S. Pat. No. 4,341,640, which discloses a process for hydrolyzing urea in waste water discharged from the production of urea into ammonia

and carbon dioxide and recovering them. According to the above patent, the urea contained in the waste water is decomposed into ammonia and carbon dioxide by hydrolysis at 120 to 250 °C, then the resulting ammonia and carbon dioxide are recovered through stripping, thus nitrous components are removed from the waste water. The process is advantageous in that both hydrolysis and stripping are conducted in a single column by integrally combining a hydrolysis reactor and a stripping column for stripping ammonia and carbon dioxide from the hydrolyzed waste water. In addition, U.S. Pat. Nos. 4,308,835 and 4,652,678 introduce a process for recovering ammonia and carbon dioxide from the urea-containing waste streams by hydrolyzing urea with increasing of temperature. Furthermore, U.S. Pat. Nos. 4,168,299 and 4,220,635 disclose a catalytic method for hydrolyzing urea, in which hydrolysis efficiency is improved with the use of a catalyst. However, the prior arts as aforementioned can hydrolyze urea, but cannot treat waste water containing refractory materials such as biuret, triuret, ammelide, ammeline, and melamine as well as urea, which are contained in waste water discharged from various processes such as a process for producing melamine.

As described above, the conventional treatment for decomposing nitrous organic components has problems in that decomposition time is too long (biological treatment), and secondary pollutants are produced and a lot of energy is consumed (incineration treatment). To avoid these problems, a process for hydrolyzing urea and recovering ammonia and carbon dioxide, which are raw materials used to synthesize urea, from the waste streams produced in the preparation of urea, has been developed. However, this process can hydrolyze nitrous organic components with low molecular weights such as urea, but cannot treat waste water containing refractory nitrous organic components such as the waste water produced from a process for producing melamine.

## DISCLOSURE OF THE INVENTION

Therefore, it is an object of the present invention to provide a process for treating waste water containing nitrous organic components, in which the nitrous organic components are hydrolyzed into ammonia and carbon dioxide, then ammonia

and carbon dioxide are separated from treated water and recovered, and the treated water is recycled, thereby environmental pollution is prevented.

Based on the present invention, the above object can be accomplished by a provision of a process for treating waste water containing nitrous organic components, comprising the steps of:

- a) feeding waste water stream to a hydrolysis reactor with the waste water stream pressurized to 130-250 atm, in which the pressurized waste water stream is heated during feeding to the hydrolysis reactor by heat exchange with the hydrolyzed stream from the subsequent step b);
- b) hydrolyzing the nitrous organic components in the waste water stream by heating the waste water stream to the liquid phase temperature range of 200-370 °C, which is below a critical point of water;
- c) transporting the hydrolyzed stream to a distillation column for recovering ammonia and carbon dioxide, in which the hydrolyzed stream is cooled during the transportation to the distillation column by heat exchange with the pressurized waste water stream to be fed into the hydrolysis reactor; and
- d) recovering ammonia as an overhead fraction, aqueous solution containing ammonia and carbon dioxide as a side fraction, and the remainder which is removed of ammonia and carbon dioxide as a bottom fraction, respectively, from the distillation column.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic flow diagram illustrating a process for treating waste water containing nitrous organic components according to the present invention.

#### BEST MODES FOR CARRYING OUT THE INVENTION

As described above, the conventional process can hardly treat waste water containing refractory nitrous organic components, for example, from a process for producing melamine. In addition, even though such nitrous organic components may be decomposed, the conventional process has problems such as discharge of secondary pollutants and excessive energy consumption.

The present invention is advantageous in that the nitrous organic components are decomposed with high efficiency; energy consumption is reduced; ammonia and carbon dioxide obtained from hydrolysis of nitrous organic components are recovered to re-use as raw materials; and the treated water is reused as process water.

Typically, the nitrous organic components decomposable in this invention may be selected from the group consisting of urea, biuret, triuret, ammelide, ammeline, melamine, cyanuric acid, and mixtures thereof, which are commonly products, raw materials or side products, generated in the waste water discharged from production processes of urea or melamine. However, it must be noted that the components as mentioned above do not limit the scope of the present invention, but are only illustrative.

The present process for treating the waste water containing nitrous organic components is roughly divided into a hydrolysis step of the nitrous organic components and a recovery step of ammonia and carbon dioxide resulting from the hydrolysis treatment.

Referring to Fig. 1, a process for treating waste water containing nitrous organic components according to the present invention is schematically illustrated.

Waste water stream 10 containing the nitrous organic components is pressurized to about 130-250 atm, preferably the pressure close to critical pressure of water (about 218 atm) with a high pressure injection pump A and fed into the heat exchanger B. When pH of the waste water stream is 7 or higher, a concentration of hydroxyl ions therein is sufficiently high to promote the subsequent hydrolysis reaction. Therefore, it is preferred that pH of the waste water stream is adjusted in the range of 7 or higher.

In the heat exchanger B, the waste water stream 11 flowing from a pump A is heated by heat exchange with a hydrolyzed stream 14 having high temperature, which



is discharged from a hydrolysis reactor D, while the hydrolyzed stream 14 is cooled. The waste water stream 12 heated in the heat exchanger B is re-heated by the heater C to a hydrolysis temperature, and then is fed into a bottom of the reactor D. To increase hydrolysis efficiency per unit volume of the reactor D, hydrolysis is conducted in a liquid phase. In this regard, the reactor D is operated under temperature and pressure of about 200-370°C under 130-250 atm. For example, when the temperature in the reactor D is lower than 200°C, a hydrolysis reaction rate is low, while when the temperature is higher than 370°C, reactants are rapidly reduced in density because reactants are under supercritical state, and so the volume of the reactor D should be increased. Furthermore, when the pressure in the reactor D is lower than 130 atm, reactants are vaporized and gas and liquid coexist in the reactor D, and thus the average density of reactant is reduced. On the other hand, when the pressure is higher than 250 atm, energy efficiency is reduced. It is preferred that the hydrolysis is carried out under the condition close to a critical point of water (374°C and 218 atm) since the nitrous organic components can be efficiently hydrolyzed in a short time.

The hydrolyzed stream 14, in which nitrous organic components are decomposed, is discharged in the liquid phase of aqueous solution containing ammonia and carbon dioxide from the reactor D through a discharge pipe positioned on the top of the reactor D. As described above, the hydrolyzed stream 14 is cooled by heat exchange with the waste water stream 11 in the heat exchanger B. Then, the stream 15 discharged from the heat exchanger B is further cooled to be near to an inlet temperature of a distillation column F for recovering ammonia and carbon dioxide by a cooler E followed by being fed to the distillation column F. In this regard, it is preferable that temperature of the stream 21 to be fed to the distillation column F is adjusted in the range of about 60-100°C.

At that time, pressure in the distillation column F is maintained in the range of about 18-21 atm, temperature at an upper part of the distillation column is about 50-60°C, temperature at a side discharging port of the distillation column is about 100-150°C, and temperature at a bottom of the distillation column is about 180-220°C.

Preferably, the distillation column F is operated in conjunction with a stripper and an absorber to recover ammonia and carbon dioxide from the hydrolyzed stream.

In the distillation column F, low boiling point materials such as ammonia and carbon dioxide ascend to the top of the distillation column F.

Meanwhile, it is difficult to separate ammonia from a mixture of ammonia and carbon dioxide because a solution of ammonia and carbon dioxide in water forms an azeotropic mixture. For this reason, the distillation column is operated in such a way that upper part of the column is maintained at an excessive concentration of ammonia by additionally supplying ammonia thereto, whereby pure ammonia 22 and 23 can be recovered as an overhead fraction. A portion of the recovered ammonia may be utilized as a reflux of the distillation column, and the remaining ammonia can be obtained as product. A solution of ammonia and carbon dioxide in water, which forms an azeotropic mixture, is discharged through the side discharging port positioned at a middle part of the distillation column, thereby recovered as a side fraction. The side fraction may be sent to a process for synthesizing urea and utilized as a raw material.

A bottom fraction 27 which is removed of ammonia and carbon dioxide is discharged through a pipe 26, and then may be recovered to re-use as process water. In the case of treating waste water generated during the production of melamine, the hydrolysis of nitrous organic components is controlled in such a way that the product melamine is slowly decomposed and thus left in the bottom fraction, thereby melamine can be reclaimed with high efficiency in a recovery process.

A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

#### EXAMPLE 1

##### Hydrolysis of a solution of urea in water

Urea of 1000 ppm was dissolved in an aqueous ammonia solution of 11 % and hydrolyzed. A hydrolysis reaction was conducted under 3700 psig with a temperature and retention time of a reactor being varied. After the hydrolysis

reaction, final urea concentration indicating a degree of hydrolysis of urea was measured. Results are described in Table 1, below.

TABLE 1

5 Conversion of urea according to reaction temperature and retention time

Reaction temp.(°C)	Retention time(sec)	Urea	
		Concentration(mg/L)	Conversion(%)
200	7	819	18.1
200	10	745	25.5
200	20	698	30.2
220	7	730	27.0
220	10	693	30.7
220	20	502	49.8
240	7	580	42.0
240	10	437	56.3
240	20	237	76.3
260	7	370	63.0
260	10	165	83.5
260	20	22	97.8

## EXAMPLE 2

10 Hydrolysis of a solution of biuret in water

Biuret of 1000 ppm was dissolved in an aqueous ammonia solution of 11 % and hydrolyzed. A hydrolysis reaction was conducted under 3700 psig with a temperature and retention time of a reactor being varied. After the hydrolysis reaction, final biuret concentration indicating a degree of hydrolysis of biuret was measured. Results are described in Table 2, below.

15

TABLE 2

Conversion of biuret according to reaction temperature and retention time

Reaction temp.(°C)	Retention time(sec)	Biuret	
		Concentration(mg/L)	Conversion(%)
200	7	860	14.0
200	10	795	20.5
200	20	640	36.0
220	7	685	31.5
220	10	602	39.8
220	20	405	59.5
240	7	608	39.2
240	10	435	56.5
240	20	180	82.0
260	7	405	59.5
260	10	204	79.6
260	20	8	99.2

EXAMPLE 3

5

### Hydrolysis of a solution of triuret in water

Triuret of 1000 ppm was dissolved in an aqueous ammonia solution of 11 % and hydrolyzed. A hydrolysis reaction was conducted under 3700 psig with a temperature and retention time of a reactor being varied. After the hydrolysis reaction, final triuret concentration indicating a degree of hydrolysis of triuret was measured. Results are described in Table 3, below.

10

TABLE 3

Conversion of triuret according to reaction temperature and retention time

15

Reaction	Retention	Triuret
----------	-----------	---------

temp.(°C)	time(sec)	Concentration(mg/L)	Conversion(%)
200	7	840	16.0
200	10	775	22.5
200	20	650	35.0
220	7	685	31.5
220	10	593	40.7
220	20	398	60.2
240	7	608	39.2
240	10	413	58.7
240	20	110	89.0
260	7	387	61.3
260	10	175	82.5
260	20	5	99.5

## EXAMPLE 4

## Hydrolysis of a solution of an ammelide and ammeline in water

5 A mixture of ammelide and ammeline of 1000 ppm was dissolved in an ammonia aqueous solution of 11 % and hydrolyzed. A hydrolysis reaction was conducted under 3700 psig with a temperature and retention time of a reactor being varied. After the hydrolysis reaction, final ammelide and ammeline concentration indicating a degree of hydrolysis of ammelide and ammeline was measured. Results are described in Table 4, below.

10

TABLE 4

Conversion of ammelide and ammeline according to reaction temperature and retention time

Reaction Temp.(°C)	Retention time(sec)	Ammelide	Ammeline
		Conc.(mg/L)	Conc.(mg/L)
200	23	381	280

200	68	416	193
200	135	438	141
220	22	310	282
220	65	330	157
220	129	319	95
240	22	315	210
240	63	237	86
240	126	178	37
260	21	262	126
260	61	131	19
260	122	55	4

## EXAMPLE 5

## Treatment of waste water discharged from a process for producing melamine

5 In a process for producing melamine, waste water was treated after melamine was recovered through a crystallization step. The waste water discharged from the process for producing melamine includes side products produced during synthesis of melamine, unreacted materials such as urea, biuret, ammelide, and ammeline, and melamine which is not crystallized nor recovered. Compositions of the waste water and the treated water after treatment of the waste water are described in Table 5, below.

10 The hydrolysis reaction was conducted under 3400 psig for a retention time of 15 min.

TABLE 5

15 Composition of the waste water discharged from the process for producing melamine, and composition of the treated water

	Concentration (mg/L)					Temp. (°C)	Organic nitrogen (mg/L)
	Urea	Biuret	Ammelide	Ammeline	Melamine		

Waste water	900.0	70.0	990.0	1710.0	7700.0	-	6957.5
Treated water 1	0.0	0.0	0.0	0.1	43.4	350	29.0
Treated water 2	0.0	0.0	0.0	0.8	79.0	340	53.1
Treated water 3	0.0	0.0	0.0	1.3	136.0	330	91.4
Treated water 4	0.0	0.0	3.0	12.0	250.0	300	174.6

From the results shown in Table 5, it can be seen that organic nitrogen is removed at 99 % or higher efficiency, and hydrolysis efficiency is increased with increasing of temperature.

#### EXAMPLE 6

##### 5 Treatment of waste water discharged from the process for producing melamine

Waste water discharged during production of melamine, which is different from that of Example 5 in terms of components concentration, was treated with varying of temperature, pressure, and retention time in a hydrolysis reactor as shown in Fig. 1. Compositions of the waste water and the treated water after treatment of the waste water are described in Table 6, below.

TABLE 6

15 Composition of the waste water discharged from the process for producing melamine, and composition of the treated water

	Concentration (mg/L)					Temp. (°C)	Press. (psig)	Time (min)
	Urea	Biuret	Ammelide	Ammeline	Melamine			
Waste	400.0	70.0	740.0	1590.0	4050.0	-	-	-

water								
Treated water 1	0.0	0.0	0.0	0.0	13.2	370	3700	15
Treated water 2	0.0	0.0	2.0	1.4	123.2	350	3700	10
Treated water 3	5.0	0.0	5.9	10.8	822.6	350	3700	5
Treated water 4	70.0	0.0	7.6	5.5	297.1	350	2000	2
Treated water 5	40.0	0.0	2.8	1.2	78.7	350	2000	3
Treated water 6	120.0	444.3	9.5	33.7	1653.0	350	2000	1/3
Treated water 7	0.0	0.0	0.0	3.1	295.8	300	3140	15
Treated water 8	0.0	0.0	0.0	4.8	373.5	300	3140	10

<sup>1</sup>Time: Retention time

From the results shown in Table 6, it can be seen that hydrolysis efficiency is increased with increasing of temperature and retention time.

#### EXAMPLE 7

##### Recovery of ammonia and carbon dioxide from treated water

5 After the waste water discharged during production of melamine was treated, and ammonia and carbon dioxide were recovered from the waste water in the distillation column. The hydrolysis reactor was continuously conducted at 330°C under 3200 psig for the average retention time of 12 min, then the hydrolyzed water was transported from the reactor to a distillation column. Ammonia was recovered  
10 through the distillation column with its top and bottom temperatures being 52 and 200°C and its pressure being 276 psig. Flow rates and compositions of hydrolyzed



stream 21, and overhead fraction 24, side fraction 25, and bottom fraction 27 of the distillation column were measured. Results are described in Table 7, below.

TABLE 7

- 5 Flow rates and compositions of hydrolyzed stream, and overhead fraction, side fraction and bottom fraction of the distillation column

Streams	Flow rate(kg/hr)	Concentration (wt %)			
		Ammonia	Carbon dioxide	Water	Melamine
Hydrolyzed stream	29000	14.07	2.13	83.78	0.02
Overhead fraction	3111	100	0	0	0
Side fraction	3000	32.3	20.6	47.1	0
Bottom fraction	22889	0.0	0.0	99.97	0.03

## COMPARATIVE EXAMPLE 1

- 10 After the waste water discharged during production of melamine was treated, and ammonia and carbon dioxide were recovered from the waste water through the distillation column. The treated water according to Example 7 was compared with the treated water according to the conventional process in terms of the composition of an inlet stream (A), overhead fraction (B), side fraction (C), and bottom fraction (D) of the distillation column, respectively. Results are described in Table 8, below.

15

TABLE 8

	Conventional process				Example 7			
	A	B	C	D	A	B	C	D
Rate(kg/h)	31000	2762	2600	25638	29000	3111	3000	22889
Conc.(wt%)								
Water	84.9	0.0	45.4	98.10	83.78	0.0	47.10	99.97

CO <sub>2</sub>	0.6	0.0	7.2	0.0	2.13	0.0	20.6	0.0
Ammonia	12.9	100.0	47.4	Trace	14.07	100.0	32.3	Trace
Ammelide	0.13	0.0	0.0	0.16	0.0	0.0	0.0	0.0
Ammeline	0.16	0.0	0.0	0.19	0.0	0.0	0.0	0.0
Melamine	0.96	0.0	0.0	1.16	0.02	0.0	0.0	0.03
Urea	0.32	0.0	0.0	0.39	0.0	0.0	0.0	0.0

From the results shown in Table 8, it can be seen that nitrous organic components contained in the bottom fraction are removed at 99 % or higher efficiency and recovered in a form of ammonia and carbon dioxide in the case of the present invention. Further, the recovery of ammonia is increased from 2,762 to 3,111 kg/hr, i.e. by 12.6 %.

#### INDUSTRIAL APPLICABILITY

As described above, the present invention provides a process for treating waste water containing nitrous organic components. The nitrous organic components are hydrolyzed under conditions of temperature and pressure close to a critical point of water, and so organic components in the waste water are decomposed into ammonia and carbon dioxide, then ammonia and carbon dioxide are recovered for using as raw materials. The present invention is advantageous in that nitrous organic components discarded as waste materials can be recycled in the form of ammonia and carbon dioxide capable of being used as raw materials by hydrolyzing nitrous organic components contained in the waste water to ammonia and carbon dioxide at 99 % or higher efficiency, and the treated water which is removed of nitrous organic components is reutilized as process water. Furthermore, the present invention can be usefully applied to processes discharging nitrous organic components in large quantities such as a process for producing melamine or urea, thereby preventing waste water containing nitrous organic components from being released to the environment.

It is thus seen that the objects set forth above, as made apparent from the preceding description, are efficiently attained and, since certain changes may be

made in carrying out the above method and in the construction set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the accompanying drawing shall be interpreted as illustrative, and not in a limiting sense.

## CLAIMS

1. A process for treating waste water containing nitrous organic components, comprising the steps of:

5 a) feeding waste water stream to a hydrolysis reactor with the waste water stream pressurized to 130-250 atm, in which the pressurized waste water stream is heated during feeding to the hydrolysis reactor by heat exchange with the hydrolyzed stream from the subsequent step b);

10 b) hydrolyzing the nitrous organic components in the waste water stream by heating the waste water stream to the liquid phase temperature range of 200-370°C, which is below a critical point of water;

c) transporting the hydrolyzed stream to a distillation column for recovering ammonia and carbon dioxide, in which the hydrolyzed stream is cooled during the transportation to the distillation column by heat exchange with the pressurized waste water stream to be fed into the hydrolysis reactor; and

15 d) recovering ammonia as an overhead fraction, aqueous solution containing ammonia and carbon dioxide as a side fraction, and the remainder which is removed of ammonia and carbon dioxide as a bottom fraction, respectively, from the distillation column.

20 2. The process according to claim 1, wherein pH of the waste water stream fed into the hydrolysis reactor is 7 or higher.

3. The process according to claim 1, wherein the hydrolyzed stream is adjusted to a temperature of 60-100°C, and then transported to the distillation column, said hydrolyzed stream being discharged from the hydrolysis reactor in the liquid phase of aqueous solution containing ammonia and carbon dioxide.

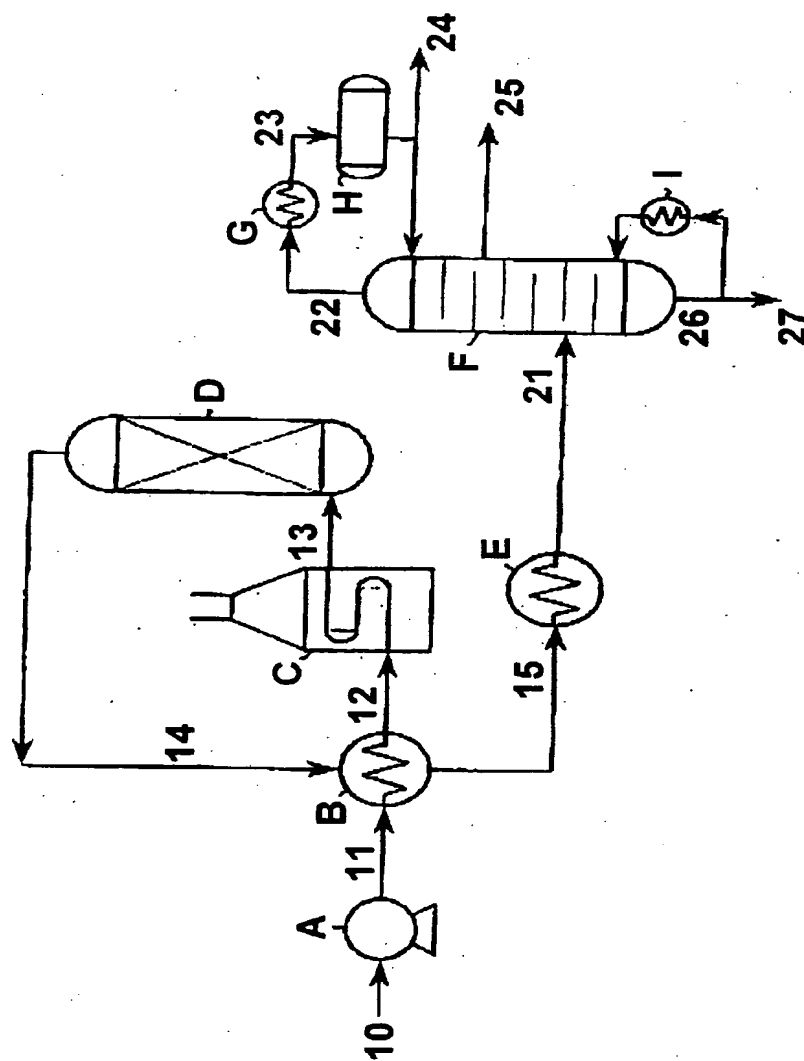
25 4. The process according to claim 1, wherein the nitrous organic components are selected from the group consisting of urea, biuret, triuret, ammelide, ammeline, melamine, cyanuric acid, and mixtures thereof.

5. The process according to claim 1, wherein the pressure of the distillation column is maintained in the range of 18-21 atm; and the temperature at the upper part, the side discharging port and the bottom of the distillation column is maintained in the range of 50-60 °C, 100-150 °C and 180-220 °C, respectively.

5        6. The process according to claim 1, wherein the distillation column is operated in such a way that the upper part of the column is maintained at an excessive concentration of ammonia by additionally supplying ammonia thereto, whereby pure ammonia may be recovered as the overhead fraction


10       7. The process according to claim 1, further comprising supplying the bottom fraction as process water.

FIGURE  
FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR02/00592

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC7 C02F 1/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC7 C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
korean patents and applications for inventions since 1975 korean utility models and applications for utility models since 1975		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
KIPASS ,PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,652,678 A( STAMICARBON B.V ) 24 March 1987 see the whole document	1 - 7
A	US 4,341,640 A( STANDARD OIL CO ) 27 July 1982 see the whole document	1 - 7
A	NL 8006477 A(UNIE VAN KUNSTMESTFABRIEKEN B.V ) 16 June 1982 see the whole document	1 - 7
A	JP 2000237761A2(KIKAIKAGAKUKENKYUSHO ) 05 September 2000 see the whole document	1 - 7
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search		Date of mailing of the international search report
12 JULY 2002 (12.07.2002)		15 JULY 2002 (15.07.2002)
Name and mailing address of the ISA/KR		Authorized officer
 Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140		HONG, Soon Chil Telephone No. 82-42-481-5542

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR02/00592

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4,652,678 A	24-3- 87	DE 66906 R4 EP 66906 B1 JP 57193439 A2	19860115 19860115 19821127
US 4,341,640 A	27-7-82	NONE	
NL 8006477 A	16-6-82	NONE	
JP 2000237761 A2	05-9-2000	NONE	



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

THIS PAGE BLANK (ISPTO)